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THE MEASUREMENT OF OSMOTIC PRESSURE AND ITS APPLICATION TO A STUDY OF AQUEOUS PHENOL SOLUTIONS

DISSERTATION

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TABLE OF CONTENTS

Acknowledgement

I. Improvements in the Mode of Measurement of Osmotic Pressure.

Introduction 1

The Cells and Membrane

Preparation of the Cells 3

Relation of Cell and Membrane 4

Cell Filling 5

Membrane Deposition 9

Discussion of the Cells 10

A New Interferometer Cell for Use as a Pressure Gage.

The Measurement of Pressure 11

Description of the Instrument 13

Cross Section of Pressure Tube - Plate 2

The Accuracy of the Instrument 14

Conclusion 16

Summary 17

Table of Contents Continued.

II. The Osmotic Pressure of Aqueous Phenol Solutions at 30° C.

Introduction 18

Experimental Results

Method Employed 20

Results, Table I 21

Discussion of Results

Comparison with Theoretical, Table II . 23

The Degree of Association of Phenol ... 27

Effect of Temperature on the Association of Phenol 29

Summary 30

Biography 31

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PART I

IMPROVEMENTS IN THE MODE OF MEASUREMENT OF OSMOTIC PRESSURE.

THE MEASUREMENT OF OSMOTIC PRESSURE AND ITS APPLICATION TO A STUDY OF AQUEOUS PHENOL SOLUTIONS.

I

IMPROVEMENTS IN THE MODE OF MEASUREMENT OF OSMOTIC PRESSURE.

INTRODUCTION.

Of the various experimental physico-chemical methods, none is of greater importance and general applicability than the measurement of osmotic pressure. The thermodynamic considerations of solutions are based on the concept of an osmotic pressure and all other properties of solutions are derivable from osmotic pressure data. Of paramount importance is the fact that osmotic pressure measurements are capable of the greatest refinement, being measurable with an extreme accuracy. Though we possess other accurate modes of measurement such as freezing point and vapor pressure, these are very limited, the former being confined to one temperature, the latter over a limited temperature range. Osmotic pressure measurements on the other hand, can be carried out with equal precision over the range of temperature at which the solvent in question exists in the liquid form and throughout all possible concentration limits.

Despite these desirable conditions and advantages,

measurements of osmotic pressure have been limited to a few substances, sugar, glucose, etc. Substances of smaller atomic weight and especially electrolytes have defied measurement and it has usually been assumed in the case of electrolytes that their measurement is impossible due to the destructive effect on the semi-permeable membrane and the permeability of the latter to such substances.

The object of this investigation was so to modify the present mode of measurement as to make it more widely applicable and if possible to apply it to the measurement of electrolytes.

THE CELLS AND MEMBRANES.

Of primary importance in the experimental determination of osmotic pressure is the character of the clay cell used as the support of the semipermeable membrane. Indeed, the lack of cells of proper texture was the cause of failure by early investigators. The cells used by Morse and Frazer in their classic work were made with every precaution to obtain a final product having a uniform porosity, a fine structure, and lacking, above all, any "air blisters". Such cells were obtained in the laboratory by carefully elutriating and washing the clays, pressing the obtained mixture, and finally turning to the required form on the lathe, after which the cell was baked and its collar glazed. The microscopic structure of such a cell is shown in Fig. 1 of Plate I. It will be noticed how fine and uniform a texture it presents.

Since the function of the cell in measurements of osmotic pressure is to secure a support for the membrane to be used, it is perfectly obvious that the fineness of texture of the latter will depend entirely on the size of the pores of the cell itself. If there should happen to be a point where the cell wall is highly porous, the membrane, if deposited at all over this area, must necessarily be held but loosely and

Fig. 1.

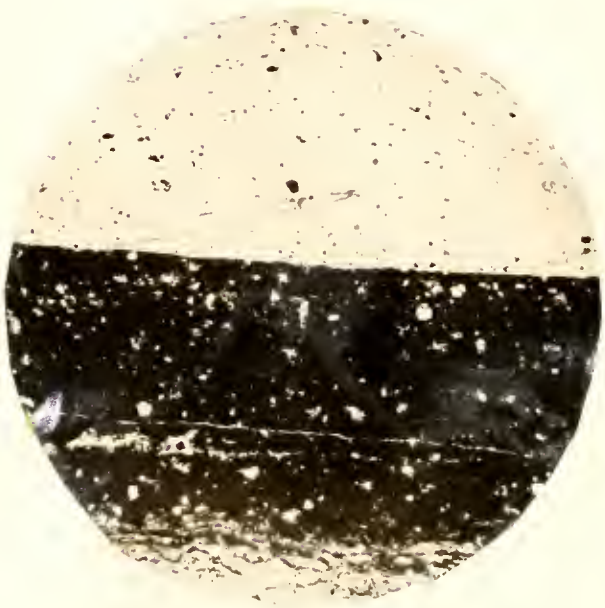

Fig. 2.

the exertion of any pressure at this point would easily disrupt it.

The failure of early attempts to measure the osmotic pressure of solutions of electrolytes was usually attributed to the destructive effect of the electrolytes on the colloidal nature of the copper ferro cyanide membrane. To be sure, this is an important factor in such determinations, but it appeared likely that the failure of early attempts was due also, in a large measure, to the character of the cell itself. The fact that only substances of high molecular weight could be studied while other materials of molecular weights of a lesser magnitude including electrolytes, passed through the semi-permeable membrane suggested that cells of a finer structure might support membranes of a finer structure which though incapable of prolonged existence in the presence of disrupting agencies, would, nevertheless, prevent leakage of the solute and thus serve as truly semi-permeable materials for the period of time required to make a measurement.

To obtain cells with a texture finer than the one shown in Fig. i, by the method described above is scarcely possible. In its preparation this cell was subjected to a pressure of about 20 tons per square inch of surface of clay for 15 hours.

Moreover, as shown later, cells of any appreciable thickness of finer texture than that shown in Fig. 2, although capable of supporting a membrane impervious to the solute would, nevertheless, fail to give accurate osmotic pressure measurements. It was decided, therefore, to produce in the cells heretofore used some insoluble material which would give a support for the membrane. Figures 2 to 6 are microphotographs of cross sections of cells so prepared. The darker areas in these sections represent the areas where the interior of the cell has been modified by the introduction of these fillings, whose extremely fine structure is shown by the opaqueness to light which these sections show under the microscope. The cells were filled in the following manner:

Figure 2.

This cell, whose cross section is shown here, was filled with magnesium silicate by electrical diffusion. The cell to be treated is placed in an apparatus similar to that used in depositing the membrane, and a current (taken directly from the lighting circuit) is passed between a roll of platinum foil placed within the cell, which serves as the anode, and a foil (2 cm. wide) which surrounds the cell, dilute solutions of $Mg(NO_3)_2$ and Na_2SiO_3 serving as anolyte and catholyte respectively. In this manner, the required filling can be ob-

tained in any thickness required, depending on the period of deposition. The optimum results are obtained with an electrolysis of about 10 hours. The initial amperage, which varies with the porosity of the cell in question, ranges from 1/2 to 1 ampere under the above conditions and drops in 10 hours to about .02 - .2 amperes. It was found that cells filled in this manner scarcely cracked on baking and gave most efficient results. After all treatments, the cells are baked in a pottery-kiln for several days at 1000°- 1450° C. and then after thorough electrolysis with a .05% Li_2SO_4 solution to completely remove all air from the cell by endosmosis, the cell is electrolyzed with pure H_2O until all electrolytes have been removed. It is then ready for the deposition of the membrane.

Figure 3.

This cell was filled in a manner similar to the preceding one, except that NaOH was used instead of the silicate and the $Mg(OH)_2$ thus formed burned in the kiln. The filling is rather narrow and not at the very surface of the cell but somewhat in the interior of the cell.

Fig. 3.

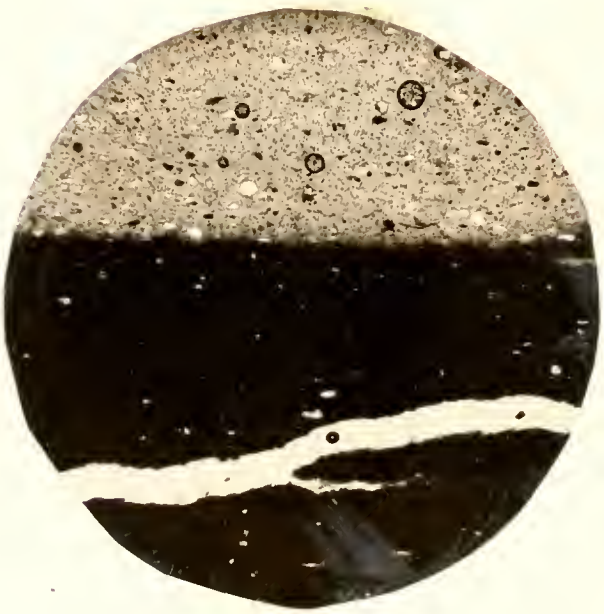

Fig. 4.

Figure 4.

This cell was filled exactly as the next one to be described but was not baked after filling. This is made evident in the photographs by the greater porosity of the baked cell due to the contracting effect of heat on the filling. The baked cells invariably gave better results which may be explained by the fact that too dense or too thick a filling does not allow free and easy diffusion of solvent through the cell, which, in turn results in a slow and incomplete attainment of equilibrium, despite the fact that with such cells none or a negligble amount of leakage occurs. The white streak in Figure 4 is due to an imperfection caused by faulty grinding.

Figure 5.

This cell contains a filling of magnesium silicate produced as follows. The cell was placed in a solution of concentrated $MgCl_2$ which diffused and thoroughly filled the pores of the cell. After washing the outer surface of the cell it was transferred to a solution of NaOH which on diffusion precipitated $Mg(OH)_2$ in the cell. In order to produce a more

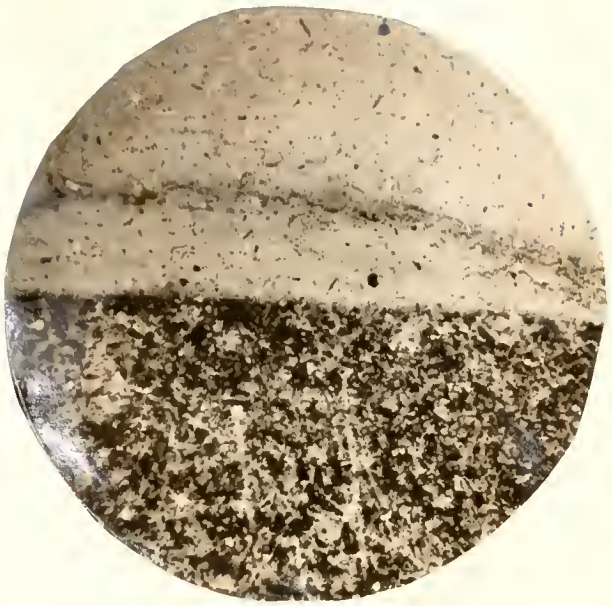

Fig. 5.

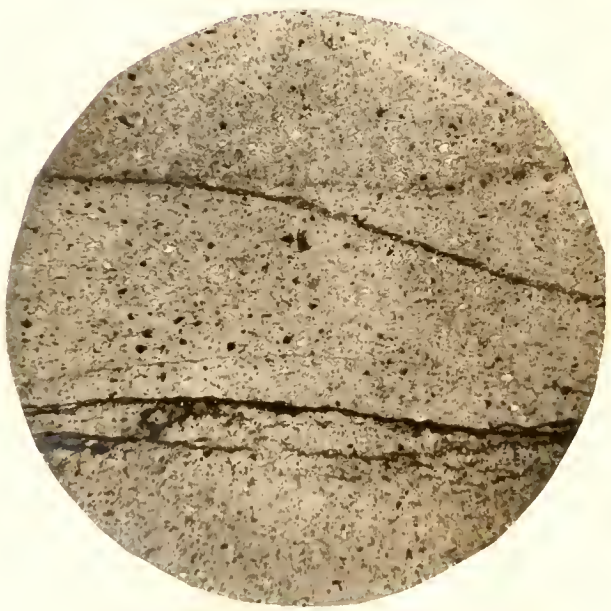

Fig. 6.

insoluble filling, this was converted to the silicate by boiling in a ten percent solution of sodium silicate. The above process was repeated several times until no more "filling" could be inserted. As seen in the photograph, the "filling" was precipitated as the outer surface of the cell where it is desired, since it is here that the membrane is deposited. The main objection to this method of cell treatment is the fact that the majority of cells so treated crack on drying.

Figure 6.

This cell was one filled by diffusion. A cell filled with $MgCl_2$ and inserted in a beaker of NaOH is allowed to stand several weeks. In this way a fine layer of $Mg(OH)_2$ is precipitated where the solutions meet which is then converted to the silicate. The cell from which this photograph was made was actually used in some quantitative measurements and gave excellent results until it cracked by the continued strain of being set up for measurement.

MEMBRANE DEPOSITION.

It was found that the optimum and quickest results are obtained, if instead of bringing about the first deposition of the membrane by means of electrolysis as is commonly done a modified form of the method described by Pfeffer[1] be used.

The cell is filled with a molar solution of $CuSO_4$ and placed in a beaker of water until the $CuSO_4$ has diffused thru the cell. The water is then replaced with a molar solution of $K_4Fe(CN)_6$, after washing the cell, and allowed to stand over night. The cell is then set up immediately with a 2 molar solution of sugar and often gives the theoretical pressure which in the case of unfilled cells can only be obtained after six months to a year of constant seasoning.

1. Osmotische Untersuchungen (1877)

DISCUSSION OF THE CELLS.

The results already obtained by the use of filled cells in the case of phenol solutions which are described in Part II and qualitative measurements made, show that the above method of cell treatment accomplishes its purpose. Regardless of the magnitude of the molecular species under consideration, the leakage in any case is but minimal. However, one point can not be too strongly emphasized, and that is the fact that non-leakage is not to be taken as a criterion of a successful measurement, as has been done by some investigators. The only criteria for a good measurement is the attainment of a pressure which remains constant for some time, non-leakage of solute and, above all, the ability to duplicate all results with other cells and measuring apparatus in so far as the limit of accuracy of the method permits. Data based on measurements not fulfilling these requirements are to be considered worthless.

Another point of superiority of the filled cells is the speed with which they attain equilibrium, which far exceeds the time required with unfilled cells. Indeed, measurements of 50 atmospheres pressure have been attained with sugar solutions, using air manometers, within 20 minutes after setting up, and the fact that in such measurements a considerable diffusion of solvent must take place to produce the pressure shows what a potent force we are dealing with.

A NEW INTERFEROMETER CELL FOR USE AS A PRESSURE GAGE.

Besides the question of cells whose improvement has been discussed above, the mode of measuring the pressure exerted, is of fundamental importance. Nitrogen filled manometers which have been used in the past have the great disadvantage that the time for equilibrium is rather long, since for its attainment, considerable solvent must pass through the cell. With electrolytes it is essential to make rapid determinations since long contact with the solutions has a detrimental effect on the membranes. Hence, a more rapidly registering pressure gage was desired. Frazer, Van Doren, Parker and Lotz[1] have devised a mode of measurement in which the change of refractive index with pressure as measured by the Zeiss Water Interferometer serves as a pressure gage. By the use of this instrument rapid determination can be made. The instrument as devised by these investigators has, however, several defects. Its construction makes it rather difficult to assemble, leakage at the glass windows being especially hard to avoid. Moreover, due to the manner in which the windows are held in place, the length of the pres-

1. J. Am. Chem. Soc. 43, 2497 (1921)

sure chamber is necessarily made small, which means a corresponding diminution in the sensitivity of the instrument, the sensitivity being directly proportional to the length of the column of liquid compressed.

The two above mentioned objections have been satisfactorily overcome by devising the modified instrument shown in Plate II. This modified form combines ease of assemblage and high sensitivity, the latter being twice that of the instrument mentioned above, As it is generally applicable whereever pressure measurements are to be quickly and accurately made, it will be briefly described.

The instrument consists essentially of a brass tube, with optical glass windows inserted at its ends, which is held in place by means of a square block of brass thru which are drilled two holes. One of these serves to hold the pressure chamber in place while the other, which is contiguous to the first, holds the other window which dipping into the water bath of the interferometer serves as the non-pressure or comparison chamber. By this arrangement only the pressure tube requires especial care in construction to avoid leakage, and it is this simplification which gives the instrument both ease in assemblage and greater accuracy. A plate screwed on the end blocks serves as a support of the chambers in the bath.

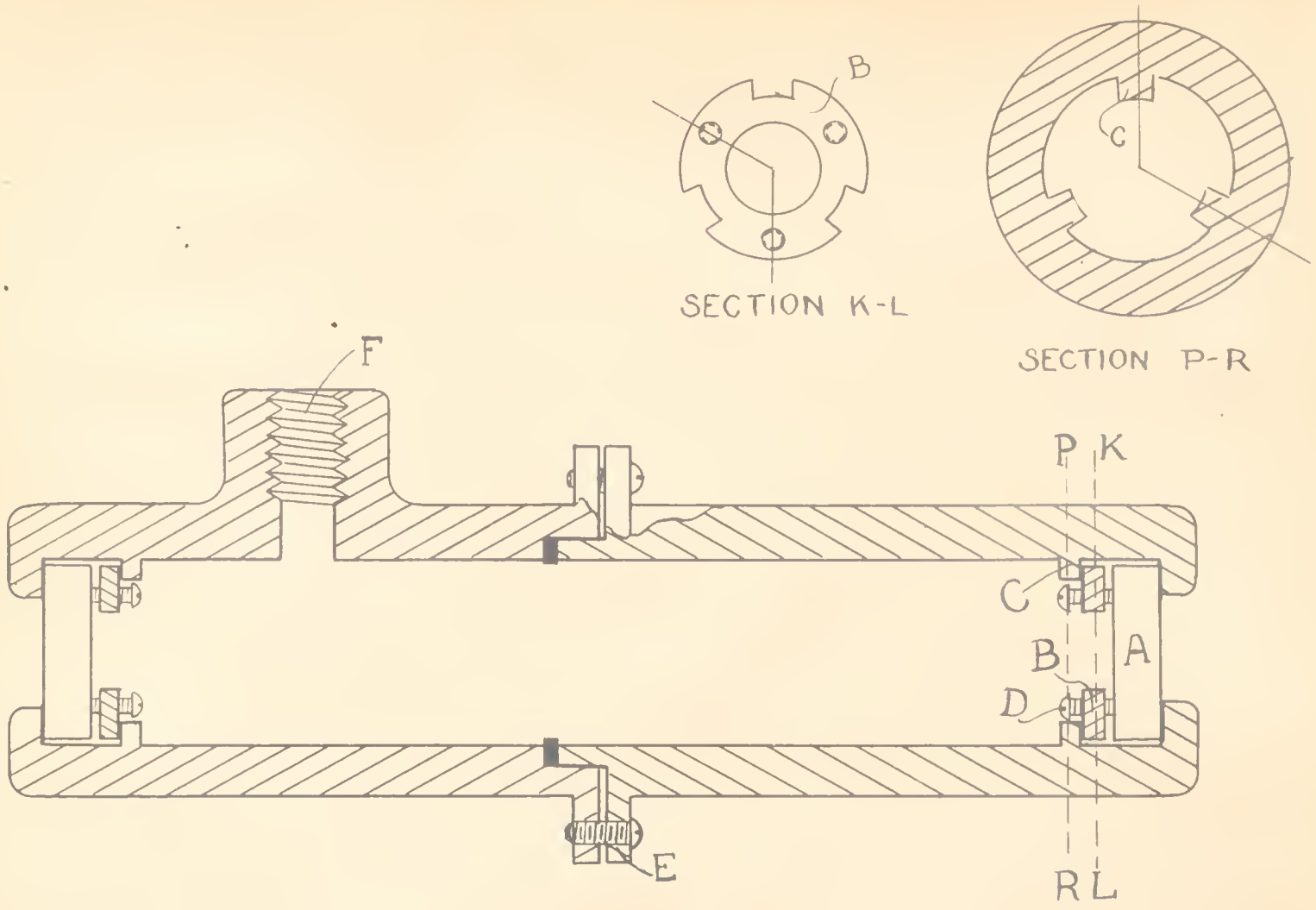

PLATE 2

Since the parts on being assembled assume the same relative position, no difficulty is experienced by a change in the zero of the instrument which would occur were the arrangement not exactly reproducible.

In order to introduce the glass windows into the ends of the pressure chambers from the inside, thus giving a tighter joint between glass and metal with increasing pressure, the pressure tube must be made in two parts. These are joined by the flange arrangements E (Plate 2), leakage being prevented by inserting a washer made of steam packing where the two ends meet within the tube. Such washers do not flow under pressure as ordinary rubber does. The tube, which is otherwise of uniform bore thruout its length, has three points of projection, C, which serve to support the washer B. The glass windows, A, are circular but have three notches corresponding to the three projections from the tube, in order that the windows may be slipped past these projections. After the windows are introduced as shown in the figure, a circular brass washer, B, having notches similar to those of the glass plate, is slipped beyond the projections, turned so that it is now supported by the projections, C, and the glass windows are held tight against their supports by means of the screws, D. The windows are made air tight by the use of a rubber solution which is vulcanized

after assembling by slow heating. The tube is joined by I to a mercury trap which in turn is connected to the pressure cell or to the source of the pressure to be measured.

The instrument as described above has a range of 30 atmospheres. This can be increased as described by Frazer, Van Doren, Lotz and Parker[1] by the use of thin glass plates inserted in the path of the beam passing through the non pressure side.

Since the range of 30 atmospheres corresponds to 3000 divisions on the interferometer and since readings on the latter are capable of duplication within 10 divisions the pressure readings are accurate to .1 of an atmosphere. The accuracy can be further increased by using a more compressible liquid than water in the instrument and interferometer bath and by the use of a longer pressure chamber and wider windows. The length of the pressure chamber of the instrument as described above was 80 mm. By arranging the mirrors and prisms of the interferometer so that there is a greater distance between the two beams, larger windows can be used in the pressure gage which insures more accurate readings.

For a complete description of the use of the interfero-

1. Loc. cit.

meter, the reader is referred to the papers by Adams[1], Cohen and Bruins[2], Löwe[3], and Haber and Löwe [4].

Due to the difficulties inherent in most methods of pressure measurements, their limited applicability and accuracy, the use of the water interferometer should prove itself a most desirable substitute for certain methods heretofore employed.

1. Adams, J. Am. Chem. Soc., 37, 1181 (1915)
2. Cohen and Bruins, Zeit. Phys. Chem. 103, 337 (1923)
3. Löwe, Chem. Ztg. 51, 405 (1921)
4. Haber and Löwe, Z. angew. Chem. 23, 1393 (1910)

CONCLUSION

It is hoped that with the above described modifications , the road is paved for the measurement of the osmotic pressure of electrolytes and other substances whose behavior in solution as shown by the osmotic pressures which they exert, may throw light on the important questions of solutions. Qualitative results obtained with LiCl, $NaNO_3$, CH_3COONa, $CuSO_4$, NaCl, C_2H_5OH, and CH_3COOH are promising and though no successful quantitative results with concentrated solutions have, as yet, been obtained, measurements of dilute solutions are now in progress, the results with phenol appearing in Part II.

SUMMARY

1. The method of experimentally determining osmotic pressures has been improved by filling the cells on which the membrane is precipitated with various silicates.

2. Such cells are efficient supporters of the membrane, allow but a minimal leakage, a rapid attainment of equilibrium, and do not require long seasoning.

3. An interferometer cell has been devised capable of acting as an accurate and quick pressure gage.

PART II

THE OSMOTIC PRESSURE OF AQUEOUS PHENOL SOLUTIONS AT 30°.

II

THE OSMOTIC PRESSURE OF AQUEOUS PHENOL SOLUTIONS AT 30°.

INTRODUCTION.

The only reference to be found in the literature of an attempt to determine experimentally the osmotic pressure of phenol solutions is that of Naccari[1], whose results being much lower than those theoretically expected and incapable of either duplication or accurate determination, were rejected by Naccari as unsatisfactory. Owing to the crudity of the method employed, which at its best would give but qualitative results, his results are of interest only from a historical standpoint.

Indeed, even with the experimental refinements of the later methods as developed by Morse and Frazer, and their coworkers, only such compounds as the sugars were capable of accurate measure ent. Failure to obtain results with substances of a smaller molecular weight were attributed to permeability of the $Cu_2Fe(CN)_6$ membrane, or to the disintegration of the latter in the presence of such substances. The improvements in cell structure which have been described, have

1. Naccari, Real. Accad. Linc. (1897) v 6, i 32-37

enabled the methods of direct osmotic pressure measurements to be applied to a variety of substances hitherto considered beyond experimental determination, with an accuracy comparable to that of the best results obtained with cane sugar.

Phenol, presenting, as it does rather anomalous behavior in aqueous solution, was chosen for measurement, to determine whether the results obtained could be corrected with its other properties. The great uncertainty existing regarding certain of its actions, as e.g. cryoscopic behavior, hydration, etc. demanded an attack from another point of view, in order to throw light on these subjects. The fact that it forms a binary mixture, was also suggestive. Moreover, all substances hitherto measured have approximated ideal solutions and obey the van't Hoff osmotic pressure law more or less closely. Phenol was, therefore, chosen, as it diverges widely from such behavior.

EXPERIMENTAL.

The measurements were carried out thruout the solubility range at 30°, with nitrogen-filled manometers in a bath constant to 0.05°C. The method was essentially that described and used by Frazer and Myrick[1] for sugar solutions, manometers being used, however, instead of the resistance method there described. For low pressures the manometric method is the most accurate though not the most convenient mode of measurement.

The solutions were analyzed with a Zeiss water interferometer which permitted an accuracy exceeding that required by the manometric readings with a cathetometer.

The cells, which were perfected in the manner described above, and upon which was deposited the usual $Cu_2Fe(CN)_6$ membrane allowed but a slight permeability of the phenol, which was finally corrected for by the analyses of the solutions. Equilibrium was obtained in less than six hours even with the most concentrated solutions.

1. J. Am. Chem. Soc. 38, 1907 (1916).

RESULTS

TABLE I

Conc. moles of phenol per 1000 gms. of H_2O	O. P. Observed in atmos.	Ratio O. P. to conc.
0.0986	1.42	1.45
0.1006	1.47	1.46
0.1992	2.73	1.42
0.1999	2.85	1.42
0.2716	3.73	1.37
0.2965	3.89	1.31
0.3831	4.90	1.28
0.5214	6.67	1.28
0.6672	8.42	1.26
0.8936	11.20	1.25

Table I gives the results obtained and these have been plotted in Fig. 7. The curve is practically linear, tending to slope slightly towards the x axis with increasing concentrations. The third column shows this tendency.

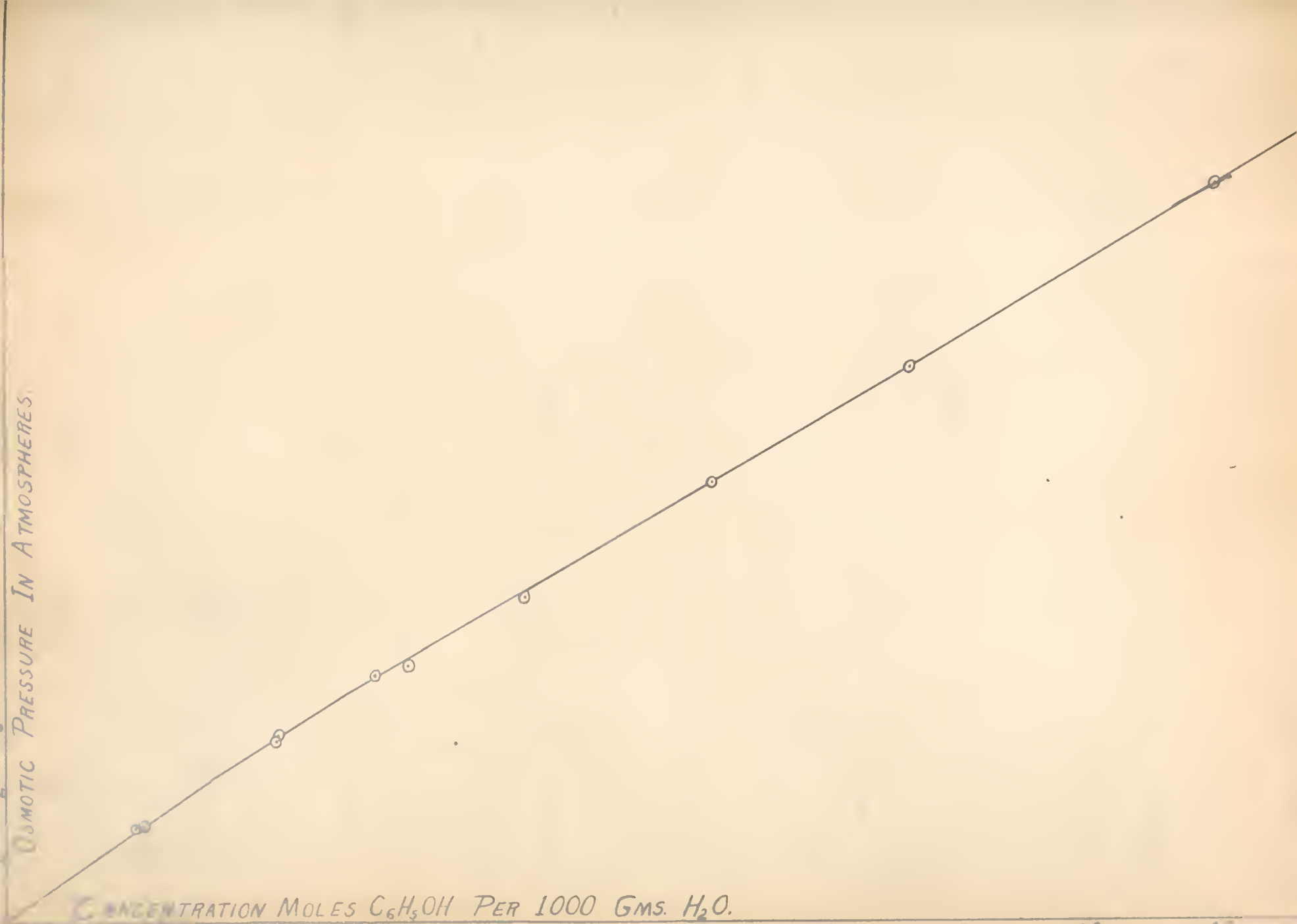
Osmotic Pressure In Atmospheres.
Concentration Moles C_6H_5OH Per 1000 Gms. H_2O.
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

Fig. 7.

From the equation for ideal solutions,

$$P = \frac{RT}{V_o}\left(x + \frac{1}{2} x^2 + \frac{1}{3} x^3 + \ldots\ldots \right)$$

where P is the osmotic pressure, V_o, the molecular volume of solvent and x, the molar fraction of solute, we can, neglecting the association of water[1] calculate the theoretical osmotic pressures of phenol solutions. This has been done in column 2 of Table II. By extrapolation of the observed values in Table I, the values for exact concentration are obtained and given in column III.

A comparison of the observed values in column 3 and the theoretical values calculated in column 2 shows, as column 3 indicates, that the former are approximately one-half the latter, thus showing the probability of association of two molecules of phenol in aqueous solution to form a diphenolic complex.

1. Kendall, J. Am. Chem. Soc. 36, 1222, 1722 (1914)
37, 149 (1915)
38, 1309, 1712 (1916)
42, 2131 (1920)

TABLE II

Conc.	O. P. calc. from formula I	O. P. Obs.	Theoret. O. P. / Obs. O. P. = degree of assoc.
.1	2.46	1.46	1.68
.2	4.92	2.84	1.73
.3	7.38	3.93	1.88
.4	9.83	5.12	1.92
.5	12.28	6.40	1.92
.6	14.73	7.62	1.93
.7	17.16	8.82	1.95
.8	19.59	10.05	1.95
.9	22.02	11.28	1.95

If χ , is the degree of association of phenol, we must introduce this factor in equation (1). Assuming the association to take place exclusively according to the equation:-

$$2\ C_6H_5OH \rightleftarrows (C_6H_5OH)_2$$

Instead of C, the molar concentration, we must use

$$\frac{\alpha c}{2} + (1 - \alpha) c$$

or $$c\left(1 - \frac{\alpha}{2}\right)$$

and x, the molar fraction becomes $\dfrac{c\left(1 - \frac{\alpha}{2}\right)}{55.5 + c\left(1 - \frac{\alpha}{2}\right)}$

Making these substitutions in equation (1) and substituting for the osmotic pressure, P, the observed values, we are able to calculate, α , the degree of association at the various concentrations. The decrease in the relatice osmotic pressures with increasing concentrations is due to an increase in the degree of association of phenol with higher concentrations. The value of α increases from 86% for .1 molar to 99% for .9 molar solutions.

Beckman and Maxim[1] have derived values for the association of phenol in carbon tetrachloride and bromoform in varying concentrations and at temperatures varying from the freezing points of the above mentioned solvents to their boiling points under normal pressure. The degree of association is found to be most sensitive to dilution, rising for example from the value 1.21 for a solution of .599 gms. of phenol in 100 grams of carbon tetrachloride at 54.1° to the value 1.58 when the same amount of solvent contains 2.738 gms. The results in Table II, column 4, derived from the osmotic pressure studies, lead us to the same conclusion, namely that dilution is a potent factor in decreasing the association ~~with solutions~~ of phenol. This decrease of association with dilution may explain the great variance in the behavior of phenol in aqueous solutions on bromination. The formation of tribrom phenol and tribrom phenol bromide (tetra brom cyclohexadienone) may be due to the presence of both the simple molecule and the associated form in solution. Attention may

1. Beckman & Maxim, Z. physik. Chem. 89, 411 (1914)

be called to alternative explanations of the above phenomena, as due to the presence of a quinoid form[1] or as due to the presence of hydrobromic acid[2].

1. Dinwiddie & Nastle, Amer. Chem. J. 46, 502 (1911)
2. J. Chem. Soc. 121, 2810

THE ASSOCIATION OF PHENOL.

The above conclusion that phenol exists in solution in an associated form is supported by its behavior in other respects, both physical and chemical. Essex[1] from a study of the compressibility of phenol, applied the principle of Tamman[2] whereby molecular magnitude of anistropic phases are determined, and finds that phenol exists as two forms of $(C_6H_5OH)_2$, a third species $-C_6H_5OH-$ being enriched at higher temperatures. Turner and English[3] found by a study of the freezing points of phenol in benzene, that its molecular weight varies from 149.6 to 194.5 which results are in the same order of magnitude as those derived from the osmotic pressure measurements. Walden[4] by a study of the specific cohesion, reaches the same conclusion. The surface tension measurements of phenol solutions[5], cryoscopic measurements, etc. all point to association of phenol.

1. Essex, Z. Anorg. Chem. 88, 189 (1914)
2. Tamman, Z. physik. Chem. 84, 293 (1913)
3. Turner & English, Proc. Roy. Soc. 105, 1786(1914)
4. Walden, Z. physik. Chem. 65, 189, 266 (1908)
5. Morgan & Adloff, J. Am. Chem. Soc. 38, 844 (1916)
Neustel, Ann. Physik. (4) 16, 61 (1905)

In its chemical reactions, also, phenol shows a tendency towards reactions not as a simple molecule but rather in an associated form. Thus the following compounds have been isolated:

$$2\ C_6H_5OH.H_2O \quad (1)$$

$$2\ C_6H_5OH.TeCl_4 \quad (2)$$

a series of compounds having the structure

$$2\ C_6H_5OH.Ca(OH)_2 \times H_2O \quad (3)$$

$$2(C_6H_5OH).H_2SO_4 \quad (4)$$

as well as numerous other addition products. In all of these compounds two molecules of phenol react pointing to the probability that phenol reacts as the dimolecular compound

$$-(C_6H_5OH)_2$$

as indicated by the osmotic pressure values.

1. Smits & Maarse, Proc. Konig. Akad. Wetan. Amsterdam, 14, 192 (1911)
Rhodes & Markley, J. Phy. Chem. 25, 527 (1921)

2. Ber. 30, 2832

3. J. Russ. Phys. Chem. Ges. 45, 1535, Zentralnlatt 1914 I 110.

4. J. Am. Chem. Soc. 36, 2507; ibid 1222. (1914).

EFFECT OF TEMPERATURE ON THE DEGREE OF ASSOCIATION.

Phenol on solution shows a marked temperature effect, the process being accompanied by a large adsorption of heat. The measurements of various properties, e.g. ebullioscopic, etc. all give results indicating a decrease in the degree of association with increasing temperature. Applying the Le Chatelier Principle, it is obvious that the compound formation must be exothermic and, vice versa, the dissociation of the double molecule takes place with an absorption of heat. We must, therefore, attribute the negative heat effect resulting on dissolving phenol as due to the breaking down of the more complicated structure with the formation of a certain percentage of simple molecules. The pure substance, therefore, exists practically entirely in an associated form and experimental studies of the molten material corroborate this, (as for example Essex's work quoted above).

SUMMARY

1. The osmotic pressure of phenol solutions have been determined thruout the solubility range at 30.0°.

2. From the results so obtained the degree of association of phenol in aqueous solution can be calculated and it is found that the percentage of simple molecules existing in the dimolecular form varies from 86% for a .1 molar solution to 98% for a .9 molar solution. The pure material is entirely associated.

3. It is suggested that the variance in the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentrations is attributable to the different molecular combinations present.

4. The great absorption of heat attending the solution of phenol is due to the partial decomposition of higher molecular forms, the reaction

$$(C_6H_5OH)_2 \qquad 2\ C_6H_5OH$$

being exothermic.

BIOGRAPHY

Arthur Grollman, the author of this dissertation, was born at Baltimore, Md., on October 21, 1901. After graduation from the Baltimore City College, he entered the Johns Hopkins University in the fall of 1918, receiving the degree of B. A. in 1920. He entered the Graduate Department of Chemistry in the fall of the same year, taking Physical Chemistry and Mineralogy as subordinate subjects. He was a recipient of Hopkins Scholarships for the years 1918- 1923 and was assistant in the physical chemistry laboratory during the spring of 1923.